ACRYLIC EMULSION COPOLYMERS FOR THICKENING AQUEOUS SYSTEMS AND COPOLYMERIZABLE SURFACTANT MONOMERS FOR USE THEREIN

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of Ser. No. 719,768 filed Apr. 4, 1985.

Alkali soluble and alkali swellable emulsion polymers and copolymers are well known (see e.g. U.S. Pat. Nos. 3,003,987; 3,070,561, and 3,081,198) and are useful in coatings, textile sizings, textile printing pastes, paints and industrial coatings where a water soluble resin can be utilized. They are also useful as thickening agents in latex based adhesives, where clays, other fillers, pigments and the like are present. In addition, alkali soluble emulsion polymers and copolymers find application in cleaners, laundry detergents, lotions, toothpastes, and other personal care products. In petroleum exploration, acrylic polymers are used as drilling fluid additives for viscosity control and as bentonite extenders for enhancing performance of the drilling fluid. Thus, according to U.S. Pat. No. 4,301,016 water soluble alkali metal polyacrylates are useful additives in drilling fluids based on fresh water.

A variety of natural and synthetic products based on cellulose, starches and proteins also have found application in paints, drilling fluids, paper coatings, adhesives, cleaners, lotions and the like. For instance, U.S. Pat. No. 3,769,247 discloses the use of certain cellulose ethers as thickeners for latex paints. Although acrylic polymer emulsions offer various advantages in most of the above-described areas of use, they have been found to be seriously deficient in some areas, particularly in water-base paint formulations where rheology control is essential to obtain correct flow and leveling, and to minimize splattering and dripping from brushes and rollers. In such paint formulations cellulose-based thickeners generally have out-performed acrylics.

In drilling muds acrylics have performed well in fresh water drilling, U.S. Pat. No. 4,301,016, supra, and U.S. Pat. No. 2,718,497, but acrylics have poor salt tolerance as compared to some cellulosic materials. On the other hand acrylics and other synthetic polymers and copolymers offer a major advantage in manufacturing reproducability, as compared to chemically grafted or modified natural products, provided the salt tolerance problem is not a factor.

The resistance of acrylic polymers to biological decay is a property which is especially beneficial in drilling muds, paints, cleaner solutions, and personal care products. In order to provide improved properties for specific applications, functional polymeric side chains have been added to synthetic acrylic systems.

In various industrial applications, acrylics available as liquid emulsions and dispersions are generally easier to use than modified natural polymers which usually are dry powders, since the former are capable of addition at most any point in a mixing process. On the other hand, dry products based on starches, cellulose, and proteins require a relatively long hydration time and take longer to dissolve than the soluble alkali metal polymers.

Another class of acrylic based emulsion polymers, popularly known as "inverse emulsions" and "inverse suspensions", such as those disclosed in U.S. Pat. Nos. 3,284,393, 3,826,771, are commercially available. These products generally rely on an organic solvent system, typically aliphatic in nature, as the continuous phase, and the presence of large quantities of surfactants. Those formulations which have greater tolerance for salt usually contain major amounts of acrylamide in the copolymers, and minor amounts of other monomers. Unfortunately, acrylamide presents a health hazard in manufacture and use of the copolymers, as well as environmental problems. The difficulty of disposal of the solvents and large amounts of free surfactants in the inverse emulsions has emphasized the need for their replacement by compositions that do not cause environmental pollution. This is especially true as regards drilling fluids where soil polution is a problem, and in the drying of coatings and adhesives where solvent evaporation contributes to air pollution.

U.S. Pat. Nos. 3,657,175 discloses improved thickening agents based on acrylics, styrene and butadiene, containing bound surfactant groups.

As shown by U.S. Pat. Nos. 4,384,096; 4,351,754, and 4,421,903, improved thickeners for aqueous systems have been developed in which there are introduced to the acrylic polymer backbones ester surfactant groups in sufficient number to enhance thickening and rheological properties. These thickeners find use in paints, coatings, adhesives, clearners, drilling fluids, textile printing inks, personal care products, and the like. Difficulties encountered in preparation of such copolymers are poor yield, inadvertant prepolymerzation, dimerization of acrylic acid monomers and the requirement of heat and vacuum conditions if complete conversion is desired. These process steps are costly to carry out, and invariably quantities of esterification catalyst and unreacted nonionic surfactant remain in the product.

In preparing the product of U.S. Pat. No. 4,421,902 a statistical mixture of acrylic acid dimer is obtained prior to esterification which interferes with yield of the desired copolymer having surfactant groups. In addition, the polymerization reaction not being quantitative, produces varying results which is undesirable in commercial practice.

A particular shortcoming of thickeners having an acrylic polymer or copolymer backbone into which are incorporated ester surfactant groups, is the tendency for the ester groups to hydrolize, especially in the presence of highly alkaline compounds, such as sodium hydroxide, whereby the thickening properties of the copolymers is substantially diminished. Thus, such acrylic copolymers do not lend themselves as effective thickeners for aqueous systems containing excess alkali.

U.S. Pat. No. 4,514,552 discloses alkali-soluble thickeners for latex paints which are emulsion copolymers of an alpha, beta-monoethylenically unsaturated carboxylic acid, a monoethylenically unsaturated monomer lacking surfactant capacity, a nonionic urethane monomer which is a urethane reaction product of a fatty alcohol or an alkyl phenol with a monoethylenically unsaturated monoisocyanate, and a polyethlenically unsaturated monomer which may be copolymerized with the copolymer. These thickeners are said to provide superior thickening action and superior hydrolytic stability as compared to the thickeners containing ester groups.

SUMMARY OF THE INVENTION

According to this invention, new anionic copolymers are prepared by emulsion copolymerizing (A) an addition copolymerizable nonionic urethane monomer